

# Optical fibre sensor for the measurement of ozone

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**Abstract.** The use of optical fibres for the measurement of ozone based on the optical absorption of both UV light at 254nm and visible light at 600nm is investigated and tested. Calculations based on the Beer-Lambert Law are also presented to demonstrate the high resolution of the UV based sensor in determining the concentration of ozone in the range of 0 mg/litre to 1mg/litre and the ability of the visible based sensor to measure high concentrations over a wide range.

## 1. Introduction

Ozone is increasingly being used for a wide range of germicidal applications, including sterilisation of water supplies, sterilisation of contaminants in controlled air supplies and environmental packaging of food products. Ozone is gradually replacing chlorine in water systems, as the products of oxidation of organic impurities are less troublesome in the case of ozone sterilisation[1]. This approach has been effective in the extermination of water-borne bacteria and viruses, e.g. cryptosporidium, which can exist in chlorinated water supplies for up to 40 minutes. The control of these processes requires that ozone concentrations be monitored in the reaction vessel and effluent. Additionally, it may be required to mount a sensor in close proximity to the ozone-producing source so that its ozone producing effectiveness can be monitored.

Ozone is often produced in electromagnetically harsh environments, e.g. near electrical discharges and the immunity of optical fibres to electrical discharges means that such a sensor may be used in a wide range of applications. Novel techniques for the generation of ozone using high power microwave plasma ultraviolet lamps[2] also renders conventional semiconductor detectors[3] useless due to the intense electromagnetic fields in their proximity. Existing optical techniques for the detection of ozone involves free space optics, which are unsuitable for accessing restricted spaces due to their unwieldy size, lack of durability and cost[4].

The work reported in this paper studies the use of optical fibres for the measurement of ozone, as it is passive (i.e. it does not contaminate its measurement environment) and it is immune from electromagnetic and chemical interference. The sensor could be retrofitted into a wide range of applications due to its small size, durability and weight. The oxygen free radicals present have a more corrosive effect on metallic objects whilst being much more passive to dielectric materials, making optical fibres the ideal basis for an ozone sensor. In this paper, an optical fibre sensor is investigated based on the optical absorption of UV light at the fundamental absorption wavelength, 254nm. The attenuation due to the ozone present is presented along with some initial calculations for determining the ozone concentrations. Initial findings of ozone sensing based on absorption in the visible region are also presented. Sensing in the visible region will allow for low cost, manageable sensors to be realised.

## 2. Experimental Set-up

The optical fibre sensor set-up consists of two fibres, an illuminating fibre connected to the light source and a read fibre connected to the spectrometer. These two fibres are connected to collimating lenses at each end of the PTFE gas cell. The OzoneLab [5] OL80A/DLS ozone analyser and generator, generates the ozone from medical grade oxygen based on high frequency corona discharge principle and passes in through the gas cell. The OL80A/DLS ozone generator has a built in microprocessor based ozone detection module working on the principle of absorption of UV light at 254nm. The DH-2000 deuterium tungsten halogen light source from Ocean Optics [6] was used throughout these experiments. It combines deuterium and tungsten halogen light sources in a single optical path, producing a stable and powerful output in the 215nm-2000nm region of the spectrum. It was necessary to include a variable attenuator to ensure that the spectrometer output signal was prevented from going into saturation. Premium-grade optical fibre assemblies were used as the illuminating and read fibres to prevent the UV radiation from affecting the transmission in the fibres by solarisation. The S2000-TR multi-channel fibre optic spectrometer from Ocean Optics was used to spectrally resolve and detect the fibre transmission so that they could be analysed. As the spectrometer captured and detected the light, the resulting spectrum was displayed in real-time on the notebook PC using Labview™. The experimental set-up used to monitor the ozone is shown in figure 1

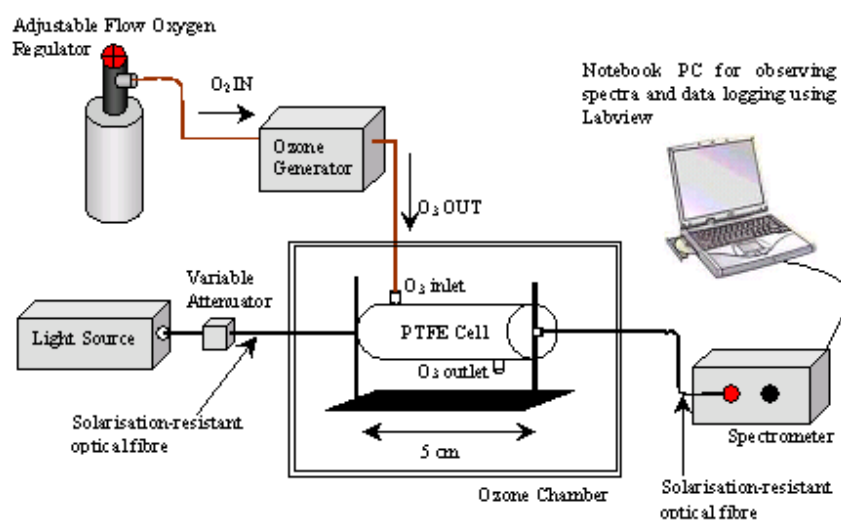
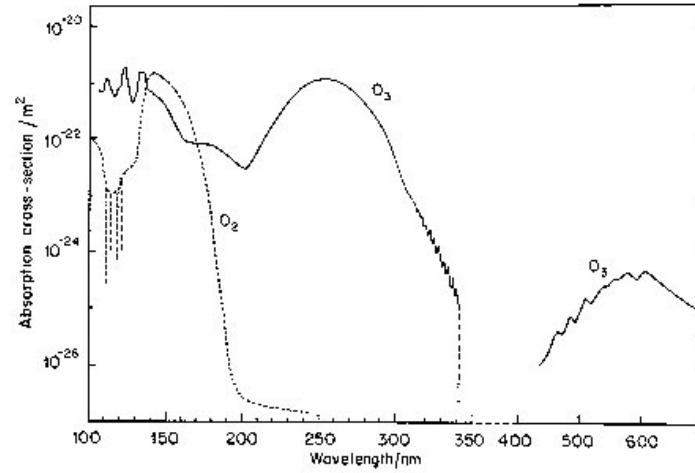


Fig. 1: Experimental set-up

## 3. Light Absorption of Ozone

If a molecule contains electrons that can resonate at a certain frequency, it absorbs light at those frequencies. Figure 2 shows the absorption cross-section for ozone. Much work has been done in the past to determine the absorption coefficients [7-10] and those determined in the ultra-violet region by Inn and Tanaka [9] and in the visible region by Vigroux [10] are considered to be the most accurate [8, 11]. Ozone absorbs UV and visible light in four main regions known as the Hartley band (spectral region: 200 - 310nm), the Huggins band (spectral region: 310 - 375nm), the Chappius band (spectral region: 375 - 603nm), and the Wulf system (spectral region: beyond 700nm). From the graph of the absorption cross-section shown in figure 2, we can see that Ozone has a high absorption region between 230nm and 270nm, with peak absorption at 253.7nm. There is also a lesser absorbing peak around 600nm, with a negligible amount of absorption observed in the 350 to 420nm region[11].



**Fig. 2.** The variations with wavelength of the absorption cross-sections of ozone. From Campbell, I. “Energy and the Atmosphere: A Physical-Chemical Approach”[12].

A variation of the Beer-Lambert Law using the Decadic Absorption Coefficient, given by the symbol  $\epsilon$ , is shown in equation 1.

$$\frac{I_L(\lambda)}{I_0(\lambda)} = 10^{-\epsilon c L} \quad \text{Equation 1}$$

where  $I_L(\lambda)$  is the intensity of light of wavelength  $\lambda$  transmitted through path length  $L$  of the medium containing concentration  $c$  of the absorbing species expressed in moles per unit volume.  $I_0(\lambda)$  is the incident intensity. The units of  $\epsilon$ , expressing  $c$  in  $\text{mol dm}^{-3}$  and  $L$  in  $\text{dm}$ , will be  $\text{dm}^2 \text{mol}^{-1}$ [12].

From this we can develop an equation to calculate the ozone concentrations from the intensity values obtained from the spectrometer. This equation is shown in equation 2.

$$C_{O_3} = \frac{-1}{\epsilon L} \log \left( \frac{I_L(\lambda)}{I_0(\lambda)} \right) \quad \text{Equation 2}$$

This gives ozone concentrations in  $C_{O_3}$  in moles per  $\text{dm}^3$ . Ozone concentrations are often expressed in the form  $\text{mg/litre}$ . A variation of equation 2 gives ozone concentration in this form and is given by equation 3.  $48 \times 10^3$  is the molar mass of ozone in milligrams/mole.

$$C_{O_3} = \frac{-48 \times 10^3}{\epsilon L} \log \left( \frac{I_L(\lambda)}{I_0(\lambda)} \right) \quad \text{Equation 3}$$

## 4. Results

### 4.1. Sensing in the UV region

The losses at 254nm, the fundamental absorption region of ozone, were compared to the losses at a non-absorbing wavelength, 400nm, and from this it was possible to measure the absorption due to the presence of ozone. Figure 3 shows the intensity at 254nm as the ozone concentration was increased and then decreased. A significant drop in intensity is evident each time the concentration was increased. After 660 seconds the ozone concentration was decreased slightly and at 700 seconds the ozone generator was switched off. These results illustrate the immediate response of the optical fibre sensor to changes in the ozone concentration. The intensity measurements in the non-absorbing region

are shown in figure 4. It is clear that the ozone has no discernible effect on the light intensity at this wavelength. The variations in intensity seen in this figure were due to system interferences, e.g. vibrations, which also affect the 254nm wavelength. In order to compensate for these interferences and intensity losses within the sensor system, the intensities at 254nm were compared by forming the ratio, as in Equation 4, with the intensities at 400nm giving a more accurate measure of the absorption due to the presence of ozone and can be seen in figure 5.

$$I_{ratio} = \frac{I_{aff}}{I_{ref}} \quad \text{Equation 4}$$

where  $I_{aff}$  is the intensity of light at the affected wavelength, i.e. 254nm, and  $I_{ref}$  is the intensity of light at the reference wavelength, i.e. 400nm.

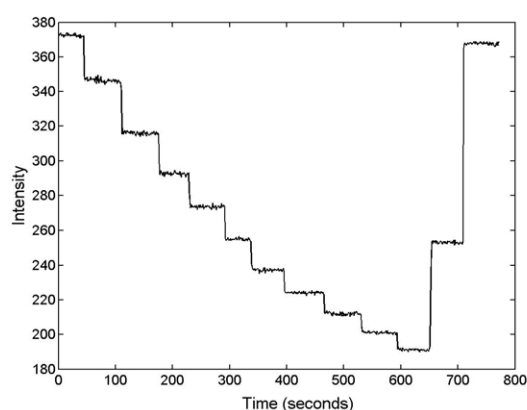


Fig.3. Intensity measurements at 254nm.

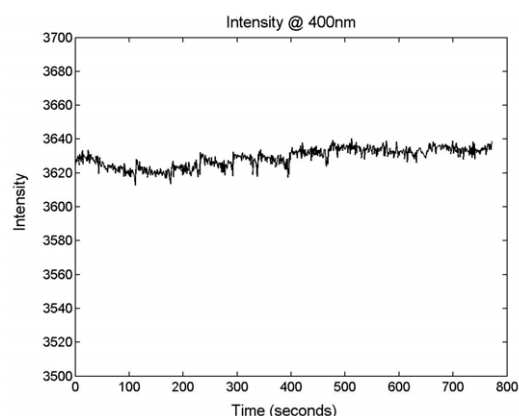


Fig.4. Intensity measurements at 400nm

Equation 3 was applied to the intensity ratio values to give the corresponding ozone concentrations in mg/litre, which are indicated on the graph in figure 5. The analyser built into the ozone generator did not have sufficient resolution to monitor the low doses, of less than 1 mg/litre, tested in this study, however figure 6 shows the calculated ozone concentrations based on equation 3 as the generators concentration regulator is increased. The Oxygen flow rate was maintained constant at a value of 1litre/min and, as expected, as the ozone concentration regulator was increased, the ozone concentration calculated from the intensity values also increased. A clearly defined step from 0.92 mg/litre to 0.97 mg/litre shows the high-resolution capabilities, 0.05mg/litre, of this system.

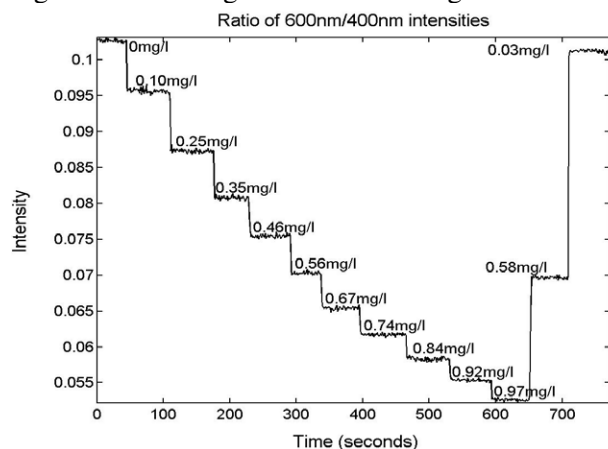


Fig.5. Ratios of intensities at 254nm and 378nm. The calculated ozone concentration in mg/litre is also shown.

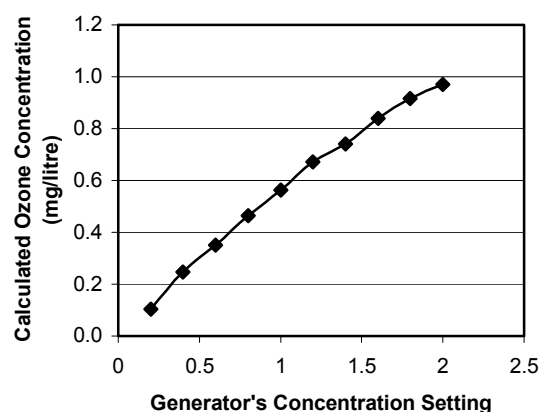


Fig.6. Calculated ozone concentration at varying concentration settings on the generator.

#### 4.2. Sensing in the visible region

The same set-up was also used to investigate absorption by ozone in the visible region at 600nm. Figure 7 and figure 8 show the light intensity at 600nm and 378nm respectively, as the ozone concentration was initially increased and then decreased. It is clear from Fig 7 that as the ozone concentration increases, the light intensity decreases. A quick recovery time is also observed as the results show an almost immediate response to the decrease in ozone concentration. The light intensity at 400nm remains largely unaffected as the ozone concentration is altered.

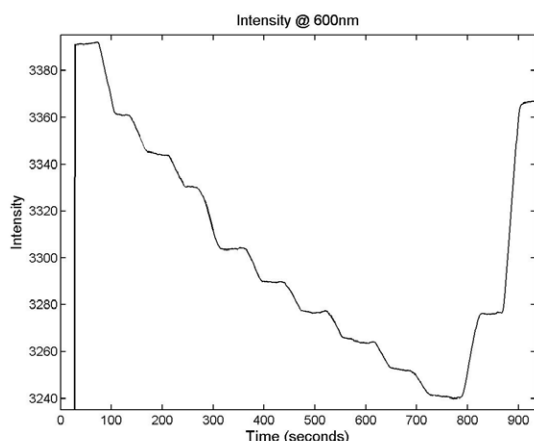


Fig.7. Intensity measurements at 600nm.

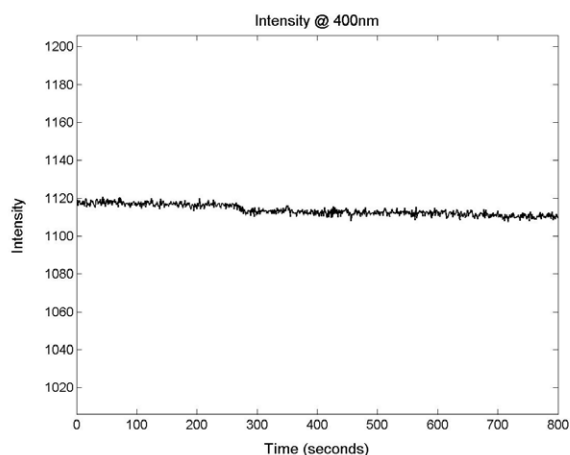


Fig.8. Intensity measurements at 400nm.

System interferences were also compensated for in the visible region by performing ratiometric analysis on the results acquired. The intensities at 600nm were compared with those at 374nm, using equation 4 and are presented in figure 9. The ozone concentrations were also calculated using equation 3 and are indicated on the graph in figure 9. Figure 10 shows the ozone concentrations calculated from the results obtained compared with those measured by the generator. The calculated concentrations are in good agreement with those measured, while a small build up of ozone within the gas cell can explain any differences observed. Further work on the design of the gas cell, to increase the flow through it, will overcome this slight variation in results. The results show a clear response to the change in ozone concentrations and show a promising comparison with the measured results. Although the resolution of this visible sensing system, 10 mg/litre, is not as high as that observed when sensing in the UV region, the wide range over which ozone concentration levels are detectable, from 0 to 138 mg/litre, makes for a very promising ozone monitoring system.

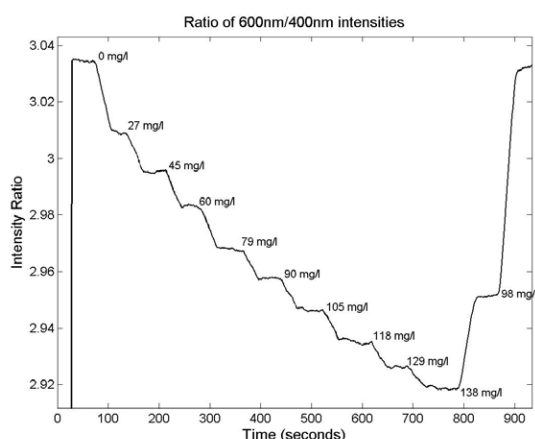


Fig.9. Ratios of intensities at 600nm and 378nm. The calculated ozone concentration in mg/litre is also shown.

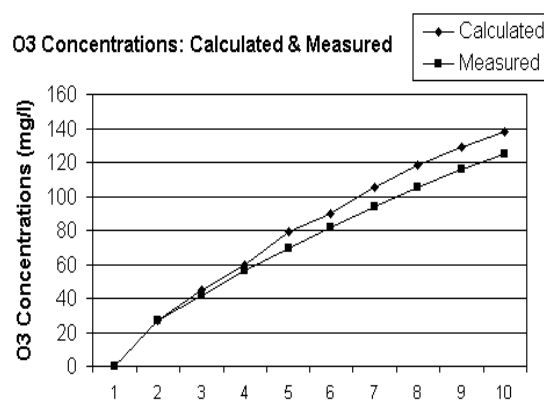


Fig.10. Comparison of the calculated and measured ozone concentrations.

## 5. Conclusions

The results obtained demonstrate the high-resolution capability, 0.05 mg/litre, of an optical fibre ozone sensor based on optical absorption at 254nm. Distinct steps were observed in the signal intensity at 254nm as the ozone concentration was increased and decreased, while at 400nm the output signal intensity remained unaffected. Due to the lower absorption by ozone at 600nm a sensor to measure high ozone concentrations has also been realised. A concentration range of between 1 mg/litre and 138 mg/litre is demonstrated here although the detection of higher concentrations may also be achieved. The results obtained show the same distinct steps as those found at 254nm, showing good resolution, 10 mg/litre, of the visible sensor at these higher concentrations. The immunity of optical fibres to electromagnetic & chemical interference and ratiometric measurements to particulate interference makes this sensor suitable for use in very harsh environments.

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